Argonne National Laboratory

INVESTIGATION OF METALLURGICAL PROBLEMS ASSOCIATED WITH THE EBR-II FUSIBLE SEALS

by

Charles C. Crothers

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) between the U. S. Atomic Energy Commission, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

INVESTIGATION OF METALLURGICAL PROBLEMS
ASSOCIATED WITH THE EBR-II FUSIBLE SEALS

by

Charles C. Crothers

EBR-II Project

September 1969

TABLE OF CONTENTS

4

LIST OF FIGURES

LIST OF TABLES

INVESTIGATION OF METALLURGICAL PROBLEMS
ASSOCIATED WITH THE EBR-II FUSIBLE SEALS

by

Charles C. Crothers

ABSTRACT

Fusible seals composed of an alloy of bismuth and tin in the eutectic ratio are used in the EBR-II rotating shield plugs. Because the seal alloy is exposed to sodium in the form of vapor or aerosol from the primary tank, the plug seals have been a continuing source of difficulty since the system became operable. We report our investigations of the solubility of sodium in the seal alloy at its normal operating temperature.

Intermetallic compounds of sodium with bismuth or tin usually have melting points above the operating temperature range of the fusible seals. The results of thermal analyses of a series of alloys containing bismuth and tin in the eutectic ratio and varying concentrations of sodium show that the solubility of sodium in busmuth-tin eutectic alloy is approximately 0.35 wt % at 177°C (350°F). Apparently solids resulting from the reaction of sodium with the seal alloy will not begin to build up in the seals until this solubility has been exceeded. Similar analyses were made of a series of alloys containing bismuth and tin in the eutectic ratio and approximately 1 wt % indium and varying concentrations of sodium. The solubility of sodium in the alloy containing indium is approximately 0.50 wt % at 177°C (350°F).

Some associated experiments concerning dross-formation rates, alloy purification, and corrosion are reported.

I. INTRODUCTION

Experimental Breeder Reactor II (EBR-II) is an important part of this nation's liquid metal fast breeder reactor program. Knowledge and experience gained from the operation and maintenance of this facility will be invaluable to the design of future reactors of this type. Reference 1 contains a complete description of the EBR-II complex.

One problem associated with a sodium-cooled reactor is containment of the coolant, which requires an inert atmosphere over all liquid-metal

surfaces. The EBR-II core and the auxiliary reactor equipment are contained in the primary tank, which also contains the bulk sodium coolant. Access through the primary-tank cover for the insertion or removal of reactor-core components is provided in part by two rotating shield plugs. The larger of these two plugs is mounted in the primary-tank cover with its axis coincident with the axis of the reactor core. A smaller rotating plug is mounted eccentrically inside the large rotating plug. This design allows the core-subassembly handling mechanism to be positioned at any desired point over the reactor core. This report explores in depth the solubility of sodium in the rotating-plug seal alloy at its normal operating temperature.

The seal between the large rotating plug and the primary-tank cover consists of a circular channel containing bismuth-tin eutectic alloy and a circular apron that dips into this channel. The channel is a part of the primary-tank cover, but the apron or dip ring is part of the rotating plug. The seal between the large and small rotating plugs is similar in design to the one between the large rotating plug and the primary-tank cover, as shown in Fig. 1.

The two seals are designed to contain the argon atmosphere of the primary tank and are completely effective only if the bismuth-tin alloy is at least partially molten at all times. However, a fully molten condition is required for plug rotation. The alloy surface in the inner annulus of each seal is protected from oxidation by the argon atmosphere of the primary tank. A secondary seal and the provision for an inert-gas purge were included in the design of the seals to prevent oxidation of the alloy in the outer annulus of each seal (see Fig. 1), but this secondary seal has been ineffective. Samples of purge gas were determined to contain a consistent 4-8% oxygen because of air in-leakage. As a result, a wet dross is formed in the channels by reaction of the alloy with oxygen. Because the secondary seal is inaccessible, correction of this condition is impractical.

Extensive examination of the wet dross showed its contents to be approximately 10 wt % tin monoxide, 80 wt % metal, and 5 wt % sodium. Sodium was analyzed as sodium carbonate, and the relative amounts of oxide and metal were first determined by passing dry hydrogen over the heated dross. The results of this analysis were subsequently verified by X-ray analysis. The X-ray analysis also verified thermodynamic theory by showing that tin is preferentially oxidized; only trace quantities of bismuth were found in the oxide.

Proper operation of the rotating seal plugs is vital to the operation of the reactor. The buildup and subsequent compacting of the wet dross in the outer annuli of the seals have, on several occasions, prevented normal rotation of the seal plugs. Compacting of the dross is enhanced because of a slight eccentricity between the dip ring and the trough. Periodic dross removal is essential for trouble-free operation.

FOR LARGE
ROTATING PLUG

T-I RING STRUCTURE

THERMOCOUPLE

AIR
FLOW

SECONDARY SEALS

LOW-OXYGEN
GAS BLANKET

LOWER-RING
HEATER

COOLING
FINS

BLADE

TROUGH

Bi - Sn ALLOY

INSULATOR
PLATE

Z-NOZZLE OF
PRIMARY TANK

AIR
FLOW

SMALL ROTATING PLUG

LOWER-RING
RETAINING BOLT

SECTION "A - A"
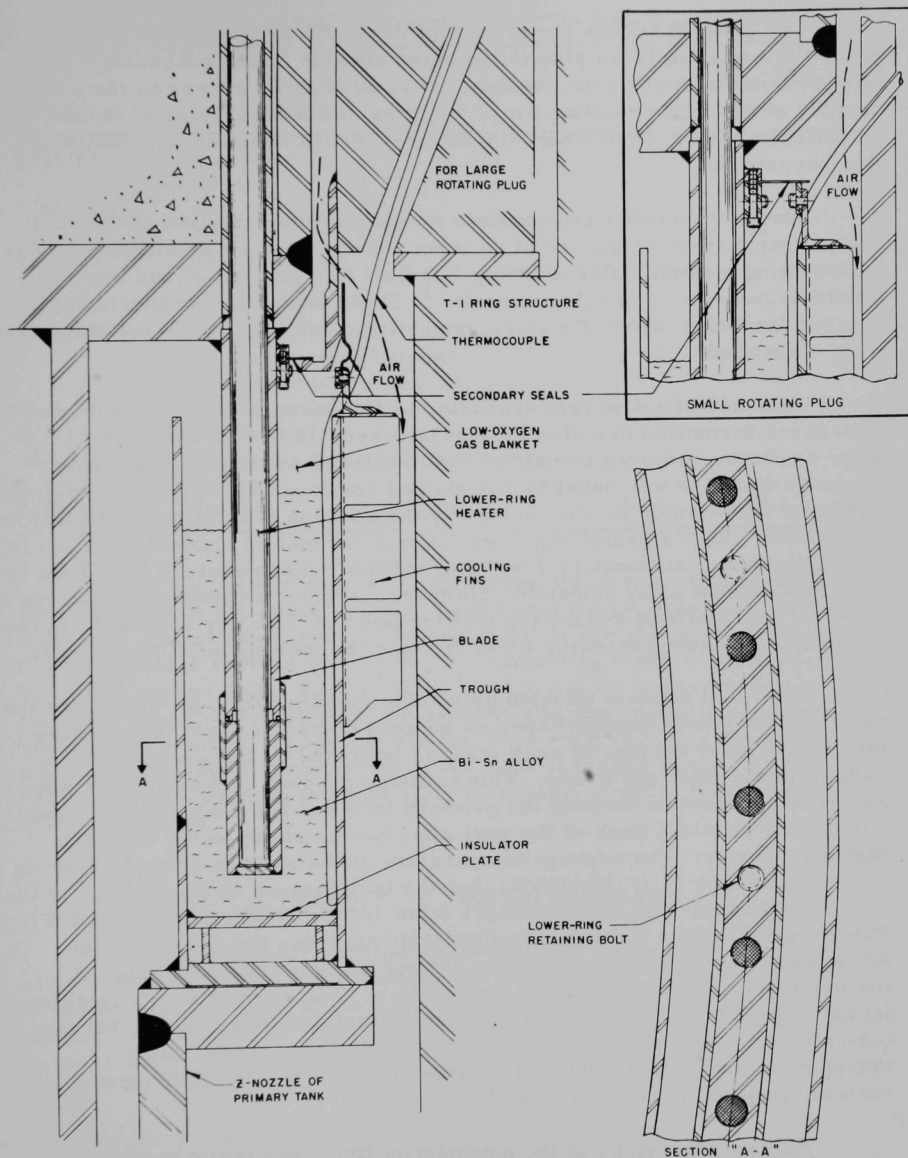
ID-103-I5199 Rev. 1

Fig. 1. Freeze Seals of Large and Small Rotating Plugs of EBR-II

To provide access for dross removal, a 7/8-in.-diam hole was drilled through the large plug to the outer annulus of the seal trough. A similar hole, with a 3/4-in. diameter, was drilled for access to the outer annulus of the small rotating plug. Because of the small size of these holes (imposed by dimensional limitations), dross removal is difficult and time-consuming.

Several methods are possible for preventing oxidation of the seal alloy. One method is the use of an inert substance, such as silicone oil, as a blanketing medium. Dow Corning 710 fluid (a silicone oil) has been extensively tested with excellent results.[2] These tests were conducted in a mockup facility in which the actual operating conditions of the rotating plugs were simulated.

The use of a different seal alloy to eliminate problems associated with dross formation has also been considered. However, the present alloy cannot be removed completely and replaced with another alloy, because an effective seal must be maintained continuously. The most desirable candidate alloy would be one formed by the addition of a third constituent to the present alloy; a promising alloy for this purpose is bismuth-tin eutectic containing small amounts (1-2 wt %) of indium.[3] The presence of indium in the alloy inhibits alloy oxidation. However, larger additions of indium (up to 25 wt %) substantially reduce the melting point of the alloy system,[4] whereas additions of indium exceeding 25 wt % cause the melting point to increase.

The seal alloy is affected by sodium contamination as well as by the oxidation reaction. Sodium vapor or aerosol transfers from the primary tank to the inner annulus of each seal, as indicated by the presence of sodium in the alloy and dross. This transfer process depends on the temperature differential between the primary tank and the seals, but the composition or physical state of the seal alloy has no effect on the rate of sodium transfer. The average temperature at the surface of the sodium in the primary tank is 371°C (700°F), but the temperature at the surface of the seal alloy in each seal trough ranges from 120°C (250°F) to 177°C (350°F). Table I summarizes the results of periodic analyses for sodium in the dross and in the seal alloy from the seal of the large rotating plug. A material balance covering about two years of reactor operation was determined in part from these analyses. The material balance shows that the rate of sodium transfer is equivalent to a sodium buildup of 3000 ± 400 ppm/yr in the seal alloy of the large trough and 1100 ± 200 ppm/yr in the seal alloy of the small trough.[2]

Sodium, dissolved in the eutectic, is first oxidized to sodium oxide; in a short time the oxide is converted to the carbonate by reaction with trace amounts of carbon dioxide in the purge gas and in the atmosphere. Sodium carbonate is undesirable because it tends to form clinker-like agglomerates when it combines with the other constituents of the dross. Trace quantities of sodium stannate and sodium bismuthate also were detected in the dross.

TABLE I. Analyses of Seal Alloy and Dross from Seal of Large Rotating Plug

Date	Sample Description	Concentration, wt %		
		Bi	Sn	Na
7/13/65	Seal alloy	59.9	43	0.166
	Dross	50.0	47	2.15
7/14/65	Seal alloy	58.8	44	0.166
	Dross	57.5	40	0.150
7/15/65	Seal alloy	59.3	45	1.510
7/16/65	Dross	42.2	-	7.5
7/20/66	Dross	42.8	-	5.5
10/6/66	Seal alloy (near surface)	59.3	-	0.15
	Seal alloy (near bottom)	59.0	-	0.175
	Seal alloy (avg of four samples)	-	-	0.176
12/6/66	Seal alloy (avg of two samples)	-	-	0.245
6/2/67	Seal alloy (avg of six samples)	-	-	0.225
12/22/67	Seal alloy (avg of two samples)	-	-	0.084
2/9/68	Dross	-	-	6.80
3/25/69	Dross	51.6	39.3	1.75

With the present method of operation, the sodium diffuses from the inner annulus to the outer annulus of each seal trough, where it is readily oxidized. The residual sodium concentration in the seal alloy remains nearly constant at about 0.25 wt %. If a blanketing medium, such as silicone oil, were applied to the surface of the seal alloy, the concentration of sodium would be expected to increase. In general, the intermetallic compounds of sodium and bismuth, or sodium and tin, have melting points above the maximum operating temperature of the EBR-II fusible seals. As the concentration of sodium in the seal alloy increases, some of these compounds may precipatate.

II. REVIEW OF THE LITERATURE

Very little direct information concerning the bismuth-tin-sodium alloy system or the bismuth-indium-tin-sodium alloy system is available in the literature. Each of the associated binary systems, however, has been studied in some detail. This section summarizes what has been reported on these alloy systems, including a discussion of segregation in a eutectic alloy.

A. Bismuth-Tin Alloy System

Figure 2 is the temperature-composition diagram for the bismuth-tin alloy system. In the liquid phase, the two constituents are completely
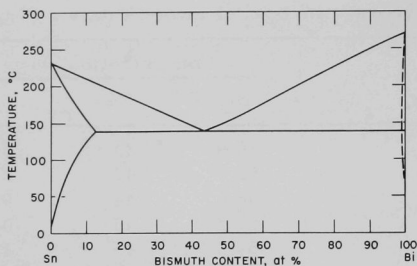
Fig. 2. Bismuth-Tin Equilibrium Diagram

miscible. No intermetallic compounds are known to exist in this system.[5] The latest work on this alloy system reports that the eutectic exists at 138.5°C and 46 at. % bismuth, based on an accuracy of ±0.05% for the determinations.[6] In this same work, the solubility of bismuth in tin is reported to be 11.9 at. % at 136°C, which is near the maximum solubility. The solubility of tin in bismuth is reported to be 3.6 at. % at 165°C. These values differ slightly from those indicated in Fig. 2 because the nominal composition of commercial alloy actually used in the EBR-II fusible seals is 43.97 at. % bismuth and 56.03 at. % tin, which is slightly different from the true eutectic composition reported in the literature.

The bismuth-tin eutectic alloy was selected as a fusible seal for EBR-II because it expands on freezing and melts at a reasonable temperature.[2] A test conducted by the Reactor Engineering Division of Argonne National Laboratory showed that the seal is not completely effective unless the alloy is at least partially molten. The most probable reason for this behavior is that Type 304 stainless steel is not wetted by the alloy at normal operating temperature (~350°F) of the seals. (See Section 1, Appendix A.)

One undesirable property of the bismuth-tin eutectic alloy in relation to its use as a fusible seal material for EBR-II is its incompatibility with 300-series stainless steels at elevated temperatures. Kassner found that the alloy preferentially dissolves nickel from the stainless steel.[7] In the operating temperature range for the EBR-II seals, however, no attack on Type 304 stainless steel has been observed.

A limited amount of information was found in the literature concerning the oxidation or dross-forming characteristics of the bismuth-tin eutectic alloy. Blumenthal et al. reported the results of a series of tests with an apparatus designed to simulate the EBR-II seal troughs.[8] Dross produced in this apparatus during 70 days of operation with commercial-grade bismuth-tin eutectic alloy was examined microscopically. Particles of the dross appeared to be essentially all metallic. Without magnification, the dross looked like a black powder. This type of dross formation has been observed in several other alloy systems. A similar examination of dross taken from the EBR-II seal troughs yielded indentical results. Figure 3 shows photographs of the dross taken with no magnification and at 375X.

From experience in the operation of the EBR-II rotating seal plugs, it can be concluded that the oxidation reaction is diffusion controlled. Essentially no dross was formed when the seals were in a molten, but static, condition. Moreover, no significant difference in the rate of dross formation

was detected with or without a nitrogen purge.[2] It is presumed that a pro-
tective layer of tin monoxide is formed at the surface of the alloy and that
this protective layer is disrupted during the rotation of the seal plugs. Some
preliminary tests of dross-formation rate are discussed in Appendix A.

.75X   375X

Fig. 3. Bismuth-Tin Eutectic Alloy Dross

B. Bismuth-Sodium Alloy System

Sodium alloys readily with bismuth to form the two intermetallic
compounds, NaBi and Na_3Bi, which have melting points of 446 and 775°C,
respectively. Figure 4 shows the
temperature-composition diagram of
this system. A freezing-point depres-
sion of 8.3°C at 3.86 at. % sodium has
been reported.[5] Similarly, a reduction
of 2°C has been observed in the eu-
tectic arrest temperature when
0.5 wt % sodium was added to the
bismuth-tin eutectic alloy.
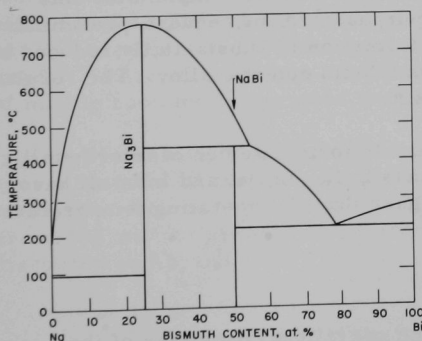
Fig. 4. Bismuth-Sodium Equilibrium Diagram[5]

C. Sodium-Tin Alloy System

Sodium alloys with tin to form
a series of intermetallic compounds.
Table II gives some physical prop-
erties of a few of these compounds.[9]
The temperature-composition diagram[5]
for the sodium-tin alloy system is given in Fig. 5, which shows the existence
of nine compounds: Na_4Sn, Na_3Sn, Na_2Sn, Na_4Sn_3, $NaSn$, $NaSn_2$, $NaSn_3$, $NaSn_4$,
and $NaSn_6$. The last four of these, in particular, are regarded as undergoing

polymorphic transformations. The others are not important in this case and have not been investigated thoroughly.

TABLE II. Physical Properties of Some Tin-Sodium Alloys

Alloy Composition	Color	Specific Gravity	Melting Point, °C	Heat of Formation, kcal
$NaSn_2$	Gray	4.725	405	15
NaSn	Gray	3.990	477	11
$NaSn_3$	Gray	3.570	478	36
Na_2Sn	Blue-Bronze	3.111	483	12
Na_4Sn	Silvery	2.315	305	21
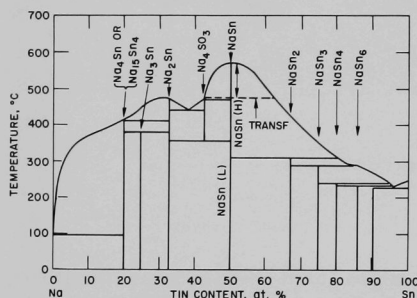
Fig. 5. Sodium-Tin Equilibrium Diagram[5]

D. Indium Alloys

Addition of small quantities of indium to various alloys increases corrosion resistance.[10] Indium has been used successfully in a number of bearing alloys to increase both wear and corrosion resistance. For this reason, the addition of indium to the bismuth-tin eutectic alloy would be expected to reduce the rate of dross formation. Darnell recommended the addition of 1 wt % indium for this purpose.[3] A subsequent, preliminary study has shown that the rate of dross formation is substantially reduced by the addition of 1 wt % indium to the bismuth-tin eutectic alloy. The results of this study are discussed in Appendix A.

Sodium alloys readily with indium to form a series of intermetallic compounds. The intermetallic compounds In_3Na, In_2Na, and InNa all have melting points that are substantially higher than the operating temperature of the EBR-II fusible seals.[11]

E. Segregation

One suggested explanation for the operational problems of the EBR-II rotating shield plugs was that eutectic segregation was occurring in the seal alloy. At the time this supposition was advanced, there was essentially no access to the seal troughs. Therefore the validity of the supposition could not be checked immediately by examining samples of seal alloy taken from the troughs. Eutectic segregation has been observed in the uranium-aluminum, silicon-aluminum, nickel-aluminum, and tin-zinc

alloy systems.[12] In a brief study, Blumenthal et al.[8] produced segregation in commercial bismuth-tin eutectic alloy by a thermal cycling technique. More recently, Mahagin[13] completed an extensive study of segregation in bismuth-tin eutectic alloy. Repeated thermal cycling through the eutectic temperature can cause segregation in this alloy system. The bismuth-rich beta crystals concentrate at the bottom of a vessel containing the alloy, and the alpha-rich dendrites concentrate at the top.

The difference between the density of the alpha phase and the beta phase is sufficient to cause segregation. Since the concentrations in the commercial bismuth-tin eutectic alloy are slightly different from the true eutectic concentration, the probability of segregation increases. Since the temperature cycles through the eutectic temperature during normal operation of the rotating seal plugs, the suggestion that segregation was responsible for the operational problems was not surprising.

Further consideration of the normal operating procedure for the rotating plugs leads to the conclusion, however, that segregation is not likely to occur. While the reactor is operating, the upper half of the seal alloy is solid and the lower half is molten. Mixing due to convection is expected to occur in the molten half of the alloy. Earlier operating procedures for the rotating seal plugs included prolonged "soaking" of the seal alloy at higher temperatures before rotation, presumably to correct the effects of segregation. Both mixing and diffusion will oppose the segregation process. In preparation for the operation of rotating seal plugs, i.e., for fuel handling, the temperature of the seal alloy is increased to approximately 177°C (350°F). Normally, fuel handling begins as soon as the seal alloy is molten. Since fuel handling requires the rotation of the seal plugs, some mixing of the seal alloy results. This is probably the most important reason why segregation has not been detected in the seal alloy. In the segregation experiments cited,[8,13] care was taken to avoid any mixing, because even a slight amount of mixing completely prevents temperature cycling, which causes segregation.

The results of analyses of seal-alloy samples taken after gaining access to the seal troughs are given in Table I. Deviations in the concentrations of the constituents are easily explained by considering analytical precision and the preferential oxidation of tin. Analytical procedures are discussed in Appendix B.

III. EXPERIMENTAL PROCEDURE

The experimental procedure for this study consisted of determining the cooling curves for two series of alloys. The alloys of one series contained bismuth and tin in the eutectic ratio and concentrations of sodium from 0.26 to 7.03 wt %. The alloys of the other series contained bismuth and tin in the eutectic ratio as well as approximately 1 wt % indium and sodium concentrations ranging from 0.19 to 7.25 wt %.

Because of the high reactivity of sodium, the experiment was conducted in a glovebox containing an argon atmosphere. The concentrations of oxygen and water vapor in the argon atmosphere were held to less than 10 ppm and less than 6 ppm, respectively. The concentrations of these and other impurities were controlled by using a molecular sieve and an automatic purge system, with the result that no significant oxidation of the samples was observed during the experiment.

Most of the apparatus for conducting the experiment was contained in the glovebox. Access to the glovebox was provided by a gastight lock. The apparatus consisted of a standard hotplate, an insulated 500-ml stainless steel beaker and cover, a motor-driven stirrer, and a stainless-steel-clad Chromel-Alumel thermocouple with a temperature recorder. Figure 6 is a schematic diagram of the apparatus.
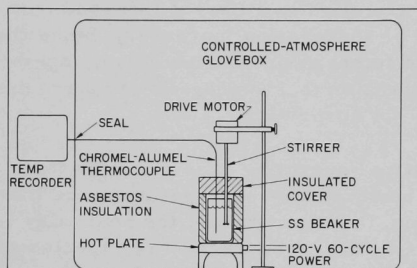
Fig. 6. Experimental Apparatus Used to Determine Alloy Cooling Curves

The thermocouple was calibrated at several different temperatures by using a precision mercury thermometer and was recalibrated by the same procedure after each cooling-curve determination. The precision of the temperature recorder was estimated to be ±3°C from information provided by the supplier. The melting point of bismuth-tin eutectic, as certified by the supplier, was 139°C (292°F); the melting point of the alloy, as determined with the experimental apparatus, was consistently within 2°C of that temperature.

The bismuth-tin eutectic, Asarcolo 281, was supplied by the American Smelting and Refining Company. Table III shows a certified composition of the eutectic alloy. Table IV shows the impurity content of reagent-grade sodium used to prepare the alloys in each series.

TABLE III. Chemical Composition of Bismuth-Tin Eutectic Alloy Used in Experiments

Element	Concentration, wt %
Bi	58.02
Sn	41.98
Fe	0.005
Cu	0.005
Pb	0.016
Ni	0.002-0.02

TABLE IV. Amounts of Impurities in Sodium Used in Experiments

Constituent	Concentration, wt %
Chloride (Cl)	0.0015
Nitrogen (N)	0.003 (max)
Phosphate (PO_4)	0.0005
Sulfate (SO_4)	0.002 (max)
Heavy metals (as Pb)	0.0005
Iron (Fe)	0.001

The bismuth-tin eutectic alloy was weighed to an accuracy of 0.01 g on a torsion-wire balance. Since the quantity of sodium used to prepare the samples was relatively small, the sodium was weighed on a four-place analytical balance. Large samples of alloy (approximately 900 g) were used to reduce the error that could result from oxidation. Since sodium is preferentially oxidized, this error could be significant.

Several trial determinations were make to check the apparatus. As a result of these trials, additional insulation was applied to the stainless steel beaker to decrease the cooling rate to approximately 3°C/min. This rate was determined to be satisfactory by comparing the cooling curves obtained from the trial determinations against those described in the literature.[14,15] Typical cooling curves experimentally obtained for a 41.88 wt % tin-57.87 wt % bismuth-0.26 wt % sodium alloy and the 41.70 wt % tin-57.61 wt % bismuth-0.68 wt % sodium alloy are shown in Figs. 7 and 8, respectively. Figure 8 also shows the corresponding heating curve. The close agreement between the arrest temperatures observed during cooling and heating is an indication of a reasonable approach to equilibrium conditions. The initial temperature for each determination was approximately 430°C. From an examination of the phase diagrams for the bismuth-sodium and the tin-sodium alloy systems, it was expected that all the thermal arrests for the alloys to be studied would occur below 430°C.
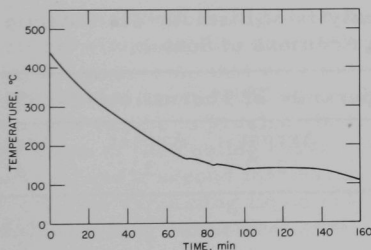
Fig. 7. Typical Cooling Curve for 41.88 wt % Tin-57.87 wt % Bismuth-0.26 wt % Sodium Alloy
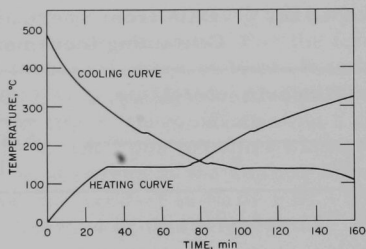
Fig. 8. Typical Cooling and Heating Curves for 41.70 wt % Tin-57.61 wt % Bismuth-0.68 wt % Sodium Alloy

Some additional tests were conducted which were concerned with rates of sodium removal from the bismuth-tin eutectic alloy, rates of corrosion, and rates of dross formation. These tests and their results are discussed in Appendix A.

IV. EXPERIMENTAL RESULTS

The data presented in this section were obtained solely from thermal analyses of the alloys. Because of the reactivity of sodium, metallographic examination of the alloys was not considered. The first series of alloys to
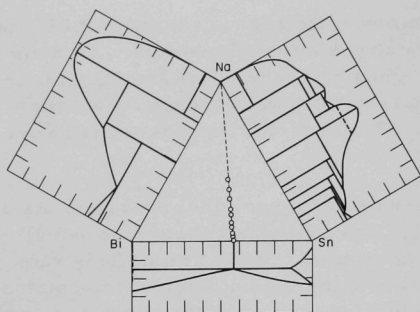
Fig. 9. Concentration Triangle for Bismuth-Sodium-Tin System

be discussed here contains bismuth and tin in approximately the eutectic ratio and with varying concentrations of sodium.

Figure 9 is a concentration triangle for the bismuth-sodium-tin alloy system with the appropriate binary equilibrium diagrams superimposed on each side. The compositions of the alloys selected for thermal analysis are indicated by open dots along the dashed line within the concentration triangle. Data from the thermal analysis of each alloy are presented in Table V. These data were used to construct the isopleth represented in Fig. 10. The dashed line of Fig. 9 is a top view of this isopleth. The methods discussed in Ref. 16 were used to construct the isopleths and isotherms for the ternary alloy systems.

The uppermost curve of Fig. 10 represents the solubility limit of sodium in the bismuth-tin eutectic alloy. The solubility of sodium in the

TABLE V. Data from Thermal Analysis of Bismuth-Tin Eutectic Containing Incremental Additions of Sodium

Composition of Alloy, at. %			Temperature of Thermal Arrest, °C			
Sn	Bi	Na	Arrest 1	Arrest 2	Arrest 3	Arrest 4
56.03	43.97	-	-	-	150	139
55.05	43.19	1.76	167	-	150	137
53.51	41.98	4.51	230	-	150	137
52.74	41.31	5.97	254	-	150	137
52.12	40.88	7.00	256	-	151	137
51.63	40.53	7.84	260	-	151	138
49.11	38.56	12.33	294	-	161	138
46.63	36.60	16.77	319	-	171	138
42.23	33.14	24.63	344	-	197	138
38.88	30.51	30.61	349	380	230	138
36.84	28.92	34.24	343	386	230	138
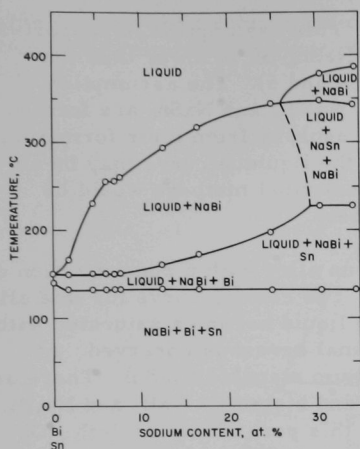
Fig. 10. Isopleth of 56 at. % Tin-44 at. %
Bismuth-Sodium System

alloy ranges from essentially zero at
139°C (282°F) to approximately 0.35 wt %
at 177°C (350°F). This temperature range
is of particular interest because in the fully
molten condition required for the rotation of
the EBR-II seal plugs, the seal alloy is
maintained at 177°C (350°F). For the reason
described on page 8, the seal alloy is
maintained in a partially molten condition
when the reactor is operating. In this condi-
tion, the temperature of the seal alloy
ranges from approximately 154°C (310°F)
at the bottom of the trough to 99°C (210°F)
at surface of the alloy. Within this temper-
ature range, essentially all the sodium
dissolved in the seal alloy will precipitate
as sodium bismuthide (NaBi). On the basis
of observations made during thermal anal-
ysis of the alloys, the sodium bismuthide
should redissolve when the seal-alloy tem-
perature is increased. Because of thermal cycling of the seal alloy, per-
manent separation of the alloy constituents should not occur.

The isopleth in Fig. 10 can be described by analyzing the behavior
of several alloys as they are cooled from the liquid state. For the first
illustration, assume that an alloy with a concentration of 10 at. % sodium
is being cooled from 300°C at which the alloy is all liquid. At 280°C, sodium
bismuthide begins to precipatate from the liquid, thereby initiating a change
in the slope of the cooling curve. At 155°C, the alloy becomes bismuth-
saturated, and a second thermal arrest is observed in the cooling curve.
At 136°C, the remaining liquid solidifies; the product is NaBi + Bi + Sn.
A relatively long isothermal arrest is observed at this temperature.

For the next illustration, assume that an alloy with a concentration
of 25 at. % sodium is being cooled from 300°C. The behavior of this alloy on
cooling is similar to the behavior of the one just described: the liquid
becomes saturated with respect to sodium bismuthide at 395°C, to bismuth
at 198°C, and to tin at 136°C. The two higher-temperature thermal arrests,
however, are more pronounced and the isothermal arrest is much less pro-
nounced than the corresponding arrests observed in the alloy containing
10 at. % sodium. This is to be expected, because at higher sodium concen-
trations, more sodium bismuthide is precipitated from the liquid, and
consequently less liquid remains at the temperature of the isothermal
arrest.

Since no thermal arrests occur within the large area labeled
LIQUID + NaBi in Fig. 10, no intermetallic compounds of sodium and tin

are assumed to be precipitated in this area. This assumption is supported by the fact that the eutectic temperature for $NaSn_6$-Sn is lower than the eutectic temperature for NaBi-Bi (see Figs. 4 and 5). The assumption should be qualified, however, because $NaSn_2$, $NaSn_4$, and $NaSn_6$ are formed by peritectic reaction, and thermal arrests resulting from their formation will be quite subtle. The slight inflection in the liquidus curve may be an indication of a sodium-tin reaction. Other analytical methods would be required to characterize the isopleth accurately.

For a third illustration, assume that an alloy with a concentration of 30 at. % sodium is being cooled from 400°C. The cooling curve for this alloy exhibits four thermal arrests. At 380°C, the liquid becomes saturated with sodium bismuthide (Na_3Bi) and the first thermal arrest is observed. At 345°C, the liquid becomes saturated with sodium stannide (NaSn). There are only two intermetallic compounds of sodium and bismuth: NaBi and Na_3Bi. Figure 4 indicates that Na_3Bi cannot exist in this part of the isopleth. On this basis, the constituent responsible for the thermal arrest must be a tin compound. At 230°C, an isothermal arrest occurs that is assumed to be the result of the transformation of sodium stannide (NaSn) to tin. This reaction may be a Class II phase reaction (see Ref. 14, p. 179). The same qualification must be applied to this assumption as in the preceding paragraph. The last remaining liquid solidifies at 136°C. The thermal arrest occuring at this temperature is quite short, indicating that very little liquid remains at this temperature.

Since the boundary between the large liquid + NaBi phase and the liquid + NaBi + NaSn phase could not be located precisely with the data available, this boundary is indicated by a dashed line in Fig. 10. The boundary, however, must be located somewhere between the data points immediately to the left and right of the dashed line and in the two solid lines between which the dashed line falls. The same reasoning applies to the boundary between the liquid + NaBi + Bi phase and the liquid + Sn + NaBi phase.

The location of the ternary eutectic for the bismuth-sodium-tin alloy system can be estimated from the available data. The binary eutectic for the sodium-tin alloy system occurs at a sodium concentration of 5 at. % (1 wt %), and the binary eutectic for the bismuth-sodium alloy system occurs at a sodium concentration of 21.8 at. % (97 wt %). From these data it is estimated that the ternary eutectic occurs at a low sodium concentration. The depression of the lower curve in Fig. 10 indicates that the ternary eutectic will most probably be located between 2 and 5 at. % sodium.

Figure 11 shows the liquidus curves for the ternary alloy system at various temperatures. The small area within which the ternary eutectic must lie is indicated by the oval dashed-line enclosure on the diagram. The eutectic will most probably occur on the tin side of the isopleth because of

the tie-line construction indicated on the diagram, but additional data points would be required for verification of this assumption.
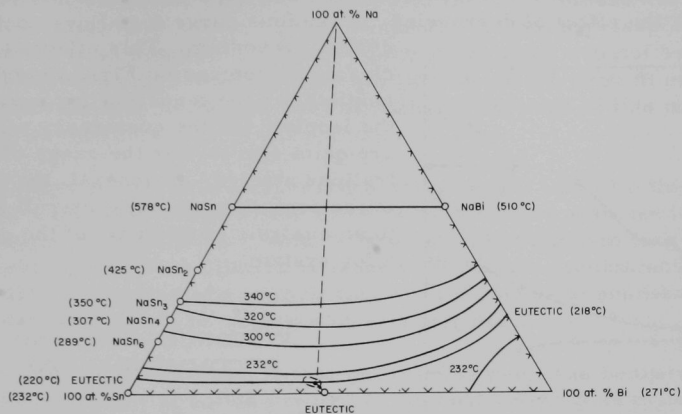
Fig. 11. Liquidus Curves at Various Temperatures
for Bismuth-Tin-Sodium Alloy System

Table VI lists data from the thermal analysis of the series of alloys containing bismuth and tin in the eutectic ratio and approximately 1 wt % indium and varying concentrations of sodium. The data from Table VI were

TABLE VI. Data from Thermal Analysis of Bismuth-Tin Eutectic
with Approximately 1 wt % Indium and
Incremental Additions of Sodium

Composition of Alloy, at. %				Temperature of Thermal Arrest, °C			
				Arrest 1	Arrest 2	Arrest 3	Arrest 4
Sn	Bi	In	Na				
55.26	43.38	1.36	-	-	-	147	139
54.52	42.80	1.34	1.34	160	-	147	136
53.16	41.74	1.31	3.79	214	-	147	136
52.40	41.13	1.30	5.17	230	-	150	136
51.82	40.67	1.28	6.23	242	-	150	136
50.38	39.58	1.24	8.80	245	-	150	134
47.90	37.60	1.19	13.31	280	-	164	134
45.50	35.72	1.13	17.65	319	-	172	134
41.90	32.90	1.04	24.17	336	-	197	125
38.72	30.39	0.95	29.94	336	382	225	-
35.58	27.92	0.88	34.52	336	392	228	-

used to construct the isopleth represented in Fig. 12. As determined by the liquidus curve of the isopleth, the solubility of sodium in the alloy is approximately 0.5 wt % at 177°C (350°F). The addition of indium to the ternary alloy has the effect of depressi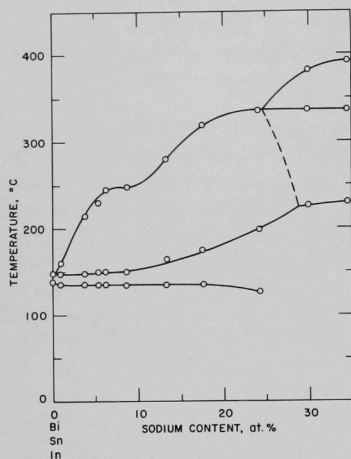ng the liquidus curve for alloys containing 2-25 at. % sodium. This effect can be seen clearly by comparing Figs. 10 and 12. The isopleth for the ternary alloy system and the isopleth for the quaternary alloy system are quite similar for the range of concentrations studied. In general, the discussion in the preceding paragraphs will also apply to an analysis of this part of the quaternary alloy system.

Fig. 12. Isopleth of 55.3 at. % Tin-
43.4 at. % Bismuth-1.36 at. %
Indium-Sodium System

V. CONCLUSIONS AND RECOMMENDATIONS

Some possible methods for improving the operation of the EBR-II rotating plugs are discussed briefly in this section. In addition, some specific recommendations are made concerning the design of fusible seals for future liquid-metal-cooled reactors.

The concentration of sodium in the EBR-II fusible seals is currently about 0.25 wt %. Assuming the use of silicone oil as a blanketing medium, the concentration of sodium in the seal alloy would build up to a concentration of approximately 0.35 wt % in four months. After the four months, precipitation of solids (NaBi) would be expected to occur at the rate of approximately 25 lb/yr. Sampling and analysis of the seal alloy are comparatively simple, and the increase in the sodium concentration in the alloy could be determined on a periodic basis.

The most convenient way to reduce the concentration of sodium in the seal alloy is by dilution with new alloy. An effective seal can be maintained with approximately one-third of the seal alloy removed from the trough. Completing two consecutive dilutions could reduce the concentration of sodium in the seal alloy to approximately 0.16 wt %, and repeating the dilution procedure at eight-month intervals could minimize the precipitation of solids. A specially designed pump has been developed to pump the alloy from the seal trough,[2] thereby facilitating the procedure for diluting the seal alloy.

Another method that has been considered for improving the operation of the rotating plugs is the addition of indium to the seal alloy. The results

of a preliminary test of dross-formation rate, discussed in Appendix A, show that the addition of a small amount of indium to the bismuth-tin alloy will reduce substantially the rate of dross formation. Sodium will be preferentially oxidized at the surface of the alloy to produce sodium carbonate as the final product. Sodium buildup in the alloy will not be expected to occur, but sodium carbonate would accumulate on the surface of the seal alloy at the rate of 5-10 lb/yr. Only preliminary studies of this method have been completed.

A more conservative approach to the problem would be the addition of indium to the seal alloy and the use of silicone oil as a blanketing medium. Since sodium is slightly more soluble in an alloy with indium than in one without indium, the first dilution to reduce the sodium concentration of the alloy would be required after approximately six months of operation. Subsequent dilutions would be required on a yearly basis.

Another consideration is that the rotating plugs can be operated with a substantial amount of solids present in the seal alloy. It is estimated that as much as 50-100 lb of solid material would not interfere with the operation of the rotating plugs. The approach described above appears to be the most promising, but a thorough engineering analysis should be completed before arriving at a final decision.

As a result of this study several recommendations can be made concerning the design of a fusible seal for future sodium-cooled reactors:

1. The compatibility of all materials in contact with the seal alloy should be studied carefully.

2. The possibility of sodium transfer to the seal alloy should be eliminated, possibly by providing a secondary seal or a cold surface for trapping the sodium.

3. Access to the seal should be considered of prime importance because of unforeseen problems that might make such access necessary.

4. The provision of an inert atmosphere for the seal alloy would be desirable, but the problem of designing a secondary gas seal is somewhat formidable. For this reason, the selection of an alloy with long-term stability is of prime importance.

APPENDIX A

Supplementary Tests and Observations

1. Corrosion

Several specimens of Type 304 stainless steel were examined after long periods of exposure to bismuth-tin eutectic alloy and to bismuth-tin eutectic alloy containing 1 wt % indium. Figure 13 is a photomicrograph of a specimen of Type 304 stainless steel after exposure to bismuth-tin eutectic alloy for 5000 hr at 177°C. The "bond" between the eutectic alloy and the stainless steel was mechanical rather than metallurgical. Figure 14 is a photomicrograph of a Type 304 stainless steel specimen after exposure to bismuth-tin eutectic alloy containing 1 wt % indium for 15,000 hr at 177°C. No "wetting" of the specimen occurred. Although these tests were conducted under static conditions, it is reasonable to assume that no corrosion (dissolution) of Type 304 stainless steel would occur as a result of exposure of either of these alloys at temperatures up to 177°C (350°F).
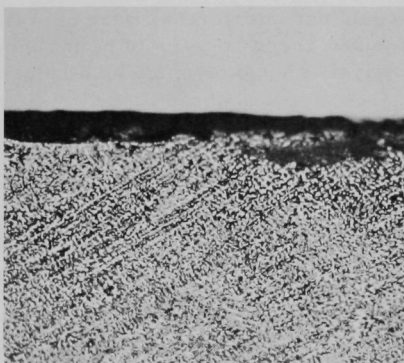
375X

Fig. 13. Type 304 Stainless Steel Specimen after 5000 hr of Exposure at 177°C (350°F) to Bismuth-Tin Eutectic Alloy

375X

Fig. 14. Type 304 Stainless Steel Specimen after 15,000 hr of Exposure at 177°C (350°F) to Bismuth-Tin Eutectic Alloy Containing 1 wt % Indium

2. Test of Dross-formation Rate

Preliminary tests of dross-formation rate were completed to determine the optimum concentration of indium for reducing the rate of dross formation in the bismuth-tin eutectic alloy. Alloy samples for this test consisted of bismuth-tin eutectic alloy and bismuth-tin eutectic alloy containing additions of 0.25, 0.50, and 1.00 wt % indium. The total weight of each sample was approximately 900 g. The samples were agitated with a motor-driven stirrer for various periods of time at a constant temperature of 177°C (350°F). The stirrer speed was approximately 200 rpm for each test. Figure 15 is a photograph of each sample after completion of the tests.
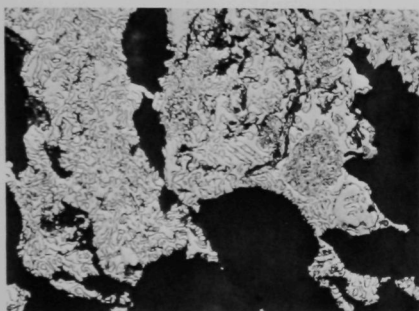
41.98 wt % Sn	41.85 wt % Sn	41.73 wt % Sn	41.48 wt % Sn
58.02 wt % Bi	57.90 wt % Bi	57.77 wt % Bi	57.52 wt % Bi
	0.25 wt % In	0.50 wt % In	1.00 wt % In

Fig. 15. Dross Formation on the Surface of Bismuth-Tin Eutectic Alloys Containing
Various Concentrations of Indium (Neg. No. ID-103-K5900 Rev. I)

375X

Fig. 16. Photomicrograph of Dross from Bismuth-Tin
Eutectic Alloy Containing 1 wt % Indium

Samples of dross from the
1 wt % indium alloy were examined
microscopically (see Fig. 16). The
character of this dross was com-
pletely different from the character of
the dross from the bismuth-tin alloy in
that no evidence of gross oxidation
could be seen microscopically. A
quantitative weight of the total dross
formed during this test could not be de-
termined because of the nature of
the dross.

The dross-formation rate for
the bismuth-tin eutectic alloy was
$0.015 \ g/cm^2/hr$; the dross-formation
rates for the alloys containing 0.25 and
0.5 wt % indium were 0.008 and 0.002 $g/cm^2/hr$, respectively. Although it can
be concluded from these tests that the optimum indium concentration for de-
creasing the rate of dross formation is between 0.5 and 1.0 wt %, additional tests
under actual, simulated EBR-II seal-trough conditions are needed.

3. Alloy Purification

A series of tests was conducted to determine if sodium could be suc-
cessfully removed from bismuth-tin eutectic alloy by preferential oxidation of
the sodium with air. Samples of alloy containing approximately 1.2 wt % sodium
were sparged with air for various periods of time. The sodium concentration in
all samples was reduced to approximately 0.40 wt % after 10 min of sparging,
but additional sparging did not reduce the sodium concentration further. The re-
sidual sodium concentration was due to occlusion of sodium oxide in the alloy.
Vibration of the samples, followed by skimming, reduced the sodium concentra-
tion to an average of 0.15 wt %. Filtration of the samples was not attempted,
but would be expected to reduce the sodium concentration still more.

APPENDIX B

Chemical Analysis

1. Bismuth Determination

     After dissolution, samples for bismuth determinations were titrated with EDTA at a pH of approximately 2.8 using thymol blue as an indicator. Tin is complexed with fluoride. The estimated accuracy for this determination is ±3%.

     Since April 30, 1968, bismuth has been determined by the atomic-absorption method with an accuracy of ±2%.

2. Tin Determination

     Tin content was determined by the fluorometric method using flavonol.[17] The estimated accuracy of this determination is ±5%. Tin has been determined by the atomic-absorption method, with an accuracy of ±2% since April 30, 1968.

3. Sodium Determination

     Sodium determinations were completed by the flame-emission-spectrophotometer method with an estimated accuracy of ±5%.

ACKNOWLEDGMENTS

I wish to express my appreciation to S. Thomas Zegler for his advice and suggestions concerning the analysis and presentation of the experimental data.

Gratitude is also expressed to Thomas R. Spalding for initiating the long-term experiments with silicone oils and indium alloys, and to Larry P. Cooper for his assistance in providing necessary experimental material and equipment.

REFERENCES

1. L. J. Koch, W. B. Loewenstein, and H. O. Monson, *Addendum to the Hazard Summary Report--Experimental Breeder Reactor-II*, ANL-5719 (Addendum) (June 1962).

2. L. P. Cooper, *Operating Experience with the EBR-II Rotating-plug Freeze Seals*, ANL-7617 (to be published).

3. R. S. Darnell, Cerro de Pasco Corporation, *Use of Indium as an Alloying Agent to Reduce Surface Oxidation*, letter to T. R. Spalding, Argonne National Laboratory (Oct. 7, 1967).

4. R. N. Lyon, Editor-in-Chief, *Liquid Metals Handbook*, NAVEXOS P-733 Rev., AEC and Department of the Navy, U.S. Government Printing Office, Washington, D.C. (1952).

5. M. Hansen and K. Anderko, *Constitution of Binary Alloys*, Second Edition, McGraw-Hill Book Company, Inc., New York (1958).

6. R. P. Eliot, *Constitution of Binary Alloys*, First Supplement, McGraw-Hill Book Company, Inc., New York (1965).

7. T. F. Kassner, *A Convective-diffusion Study of the Dissolution Kinetics of 304 Stainless Steel in the Bismuth-Tin Eutectic Alloy*, ANL-6985 (Nov 1965).

8. B. Blumenthal, L. R. Kelman, and H. V. Rhude, *Some Metallurgical Considerations in the Design and Operation of the Top Seal of EBR-II*, ANL-6837 (April 1964).

9. M. Sittig, *Sodium: Its Manufacture, Properties, and Uses*, Reinhold Publishing Corporation, New York (1956).

10. M. T. Ludwick, *Indium*, The Indium Corporation of America, New York (1959).

11. M. Heberlein, Discussion to Paper, "The Indium-Antimony System," by T. S. Liu and E. A. Peretti, Trans. Am. Soc. Metals *44*, 539 (1952).

12. B. C. Allen and S. Issero, "Segregation at the Eutectic Temperature," Acta Met. *5*, 465-472 (1967).

13. D. E. Mahagin, *An Investigation of Segregation in the Bismuth-Tin Eutectic Alloy*, a thesis for the degree of Master of Science in Metallurgical Engineering from the University of Idaho Graduate School (1965).

14. F. N. Rhines, *Phase Diagrams in Metallurgy*, McGraw-Hill Book Company, Inc., New York (1956).

15. W. C. Winegard, *Introduction to the Solidification of Metals*, The Institute of Metals, London (1964).

16. G. Masing, *Ternary Systems*, Dover Publication, Inc., New York (1960).

17. C. F. Coyle and C. E. White, *Fluorometric Determination of Tin with Flavonol*, Anal. Chem. *29*, 1486 (1957).